



Electrochemical generation and observation by magnetic resonance of superparamagnetic cobalt nanoparticles

Aliya F. Khusnuriyalova^{a, b}, Andreas Petr^{c, **}, Aidar T. Gubaidullin^a,
Aleksandr V. Sukhov^b, Vladimir I. Morozov^a, Bernd Büchner^c, Vladislav Kataev^c,
Oleg G. Sinyashin^a, Dmitry G. Yakhvarov^{a, b, *}

^a A.E. Arbuzov Institute of Organic and Physical Chemistry of the Russian Academy of Sciences, Arbuzov Street 8, Kazan 420088, Russian Federation

^b Kazan Federal University, Kremlyovskaya 18, Kazan 420008, Russian Federation

^c IFW Dresden, POB 270116, Dresden D-01171, Germany

ARTICLE INFO

Article history:

Received 13 August 2017

Received in revised form

30 November 2017

Accepted 7 December 2017

Available online 14 December 2017

Keywords:

2,2'-bipyridine

Cobalt complexes

Cobalt nanoparticles

Electrochemistry

In situ EPR spectroelectrochemistry

ABSTRACT

The electrochemical reduction of cobalt dibromide 2,2'-bipyridine (bpy) complexes (Co/bpy molar ratio 1:1) results in the formation of cobalt nanoparticles (CoNP) formed by the disproportionation reaction of the electrochemically generated cobalt(I) mononuclear complexes. The process of the electrochemical generation of CoNP was monitored by *in situ* EPR-spectroelectrochemistry where the signals of the ferromagnetic resonance (FMR) have been observed for these species. According to small-angle X-ray scattering (SAXS) analysis the average diameter and the average length of the formed cylindrical CoNP is varied from 9 to 10 nm and 30–32 nm, respectively, and correlates to the g-value and the broadness of the FMR signal observed by *in situ* EPR-spectroelectrochemistry during electrochemical process.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Currently the development of modern chemistry occurs in several priority areas, one of which is the development and the use of technology based on transition metal nanoparticles. These derivatives are widely applied in modern industry. First of all, this is due to specific properties of the nanoparticles and materials modified by them. At the present time possibilities of using metal nanoparticles in creating the new catalysts for a variety of industrial processes grow extensively. These systems obey the principles of self-assembly, which are used in a variety of technologies, applied to the fabrication of the microelectronic elements, sensoric and optical devices, the synthesis of new materials with desired properties. Transition metal nanoparticles, such as iron, cobalt, nickel, are used as catalytic agents, find applications in magnetic

recording devices, composites [1]. The cobalt complexes formed by the chelating imine ligands, including 2,2'-bipyridine, have recently become known as efficient functional materials [2] and solar cell electrolytes [3].

The problem of obtaining nanoparticles is being discussed for a long time [4–7]. The majority of the methods of preparation of nanoparticles, especially physical methods, are energy consuming and require specialized equipment. Constraints of the methods related to the difficulties in controlling the chemical composition of the product, contamination of metal nanoparticles by initial reactants. Therefore, the development of research in this area requires new methods of preparation of nanoparticles.

One perspective direction is an electrochemical process of the preparation of the nanoscale metals. The mild and one-step process conditions, that use a convenient and relatively inexpensive form of energy such as electricity are undoubted advantages of electrochemical methods. Electrochemical process for producing nanoscale metal particles in a solution is discussed in many reviews [8]. In particular, the description of electrochemical synthesis of metal nanoparticles is described in the papers [9]. Reduction of metal ions formed by dissolving the anode in the electrolyte is the basic electrochemical method. Usually the aqueous solutions are used as

* Corresponding author. A.E. Arbuzov Institute of Organic and Physical Chemistry of the Russian Academy of Sciences, Arbuzov Street 8, Kazan 420088, Russian Federation.

** Corresponding author. IFW Dresden, POB 270116, Dresden D-01171, Germany.

E-mail addresses: yakhvar@iopc.ru (D.G. Yakhvarov), a.petr@ifw-dresden.de (A. Petr).